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LARGE PERIODS IN POLYETHYLENETEREPHTHALATE FILMS[1] /1062

A. I. Kitaygorodskiy, D. Ya. Tsvankin, and Yu. M. Petrov

12371

The intensity distribution of low-angle X-ray scattering from polyethyleneterephthalate films of axially-plane texture has been investigated. The major portion of the intensities is concentrated in two domains of the reciprocal space planes. The regions have the shape of a rectangle with the large side normal to the plane of the film. The other, weaker portion of the intensity is in two regions of the surface which interconnect the long sides of the rectangle (Figure 3). The intensity distribution of the low-angle X-ray scattering was compared with the distribution of the crystallite orientation which was studied earlier with the aid of polar figures. The

comparison shows that the large period (140Å) is always observed along the axes of the macromolecules. It was also established that the domains responsible for the large periods must be regions of transition between crystallites having different orientations. The X-ray diffraction picture both at low and normal angles can be explained in terms of a system of bent and intertwined macromolecular packets. AUTHOR

In X-ray pictures of polymers taken at small angles, periods of the order of several hundred Angstrom units are observed together with continuous scattering. The investigation of this phenomenon, which was first discovered by Hess and Kiessig (Ref. 1), has been reported in many works (Ref. 2). So far, however, the origin of the large periods and their association with the structure is not clear in many respects. The well-known scheme of Hess explains the origin of the large period by the fact that along the packet of chains there is an orderly alternation of crystalline and amorphous domains. Many phenomena are difficult to understand if we proceed from this general explanation. It is not clear, for example, how the four-point, low-angle X-ray pictures occur. It is not clear why the magnitude of the large period depends on heat treatment. It seems to us that the principal shortcoming of many works devoted to the investigation of large periods and polymers is the absence of a

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12371

parallel investigation of the scattering of X-rays for small angles as well as for the normal interval of angles.

If the variation in the size or orientation of the large period is associated with the variation in the amorphous-crystalline structure of the polymer, then it is reasonable to expect that phenomena of this type will produce an effect on X-ray diffraction from the polymer at high angles. In our opinion, the parallel study of small-angle and normal-angle X-ray pictures of polymers will yield valuable information on the nature and origin of large periods.

In the present work, we compare low-angle and conventional X-ray pictures of polyethyleneterephthalate films which have an axially-plane texture. In a previous work (Ref. 3), a study was made of the distribution of the crystallite orientation in films of polyethyleneterephthalate by means of polar figures. The purpose of this work is to study the intensity distribution of low-angle scattering during diffraction from these same films. After that we shall make a comparison of the distribution of crystallitic orientation with the distribution of the intensity of low-angle diffraction. Author

Intensity Distribution of Low-Angle Scattering in Reciprocal Space

Low-angle X-ray photographs of polyethyleneterephthalate films were made with a camera having two-point diaphragms: the first was 0.2 mm and the second was 0.1 mm. The distance between the sample and the film was 250 mm. Copper radiation was used with a filter. Two series of low-angle X-ray pictures were obtained analogous to those two series which were used in constructing the polar figures in Reference 3. The first series was obtained from a pack of samples cut from the plate in the direction of the macromolecular axis. The second series of X-ray pictures was obtained with samples cut perpendicular to the axis of the chain. Each series consists of X-ray pictures obtained with successive rotations around the /1063
axis of the sample which always remains perpendicular to the incident beam of rays. In the first series of pictures, the axis of the macromolecule remains constantly perpendicular to the incident beam of rays. During the exposures of the second series the angle between the axis of the macromolecule and the beam of rays is continuously varied.

Now we present a short description of the low-angle X-ray pictures of the two series. All X-ray pictures of the first series have a dash on the first layer line (and consequently, along the negative first layer line). The length of the dash on the various X-ray pictures of each series is different. The magnitude of the large period always remains constant and is equal to 140Å. The minimum length of the dash is obtained when the incident beam is perpendicular to the plane of the film

(Figure 1a). The maximum length of the dash is obtained when the beam of rays is parallel to the plane of the film. During rotation, from one position to another, the length of the dash gradually changes (Figure 1a, b, c). The zero layer line does not exhibit either the continuous scattering or the discrete periods. When the exposure is made with a ray parallel to the plane of the film, discontinuous scattering is sometimes observed on the zero layer line (Figure 1c). If the pack of films is solidly cemented, this scattering disappears. In this case, the X-ray pictures of the first series as well as of the second series exhibit scattering only on the first layer line. In addition to this, in the case of the noncemented sample, this dash disappears at small angles between the plane of the film and the incident beam of rays. Although the origin of this diffraction effect has not been clarified completely, the facts presented show that it is not associated with the structure of the sample. Thus the intensity of the low-angle scattering is concentrated on the first layer line; i.e., on the first plane in the reciprocal space. In addition to the low-angle reflexes on the first layer lines, the X-ray pictures of the first series contain arcs which connect the ends of the reflexes on the first layer lines. These arcs are clearly visible on the X-ray picture taken with a ray perpendicular to the plane of the film,

and on X-ray pictures corresponding to rotations up to 45° from this position. For large angles, the arcs connecting the reflexes disappear. In particular, they do not appear on X-ray pictures taken with the beam parallel to the plane of the film (Figure 1c).

The X-ray pictures of the second series are different from the X-ray pictures of the first series. During successive rotations from the position where the incident beam is perpendicular to the plane of the film, the low-angle reflex is displaced towards the large angles 2θ (Figure 2a). Simultaneously, the length of the dash is decreased. For angles of rota-

tion greater than 60°, the basic reflex disappears. As far as the weak arcs which join the ends of the reflexes are concerned, they exist in all of the X-ray pictures of the second series. At high angles of rotation, when the reflex disappears, the X-ray pictures exhibit only the remnants of the arcs. Such a remnant, for example, exists in the X-ray picture of the second series taken with a beam parallel to the plane of the film (Figure 2b).

On the basis of two series of X-ray pictures, the distribution of intensity of low-angle scattering may be represented in the following manner. The principal part of the intensity is concentrated along two regions of the planes in the reciprocal space. These regions of the planes are perpendicular to the axis of the chain and correspond to the first layer lines on the low-angle X-ray picture of the textures. In appearance, the regions of the planes are approximately rectangular. The long side of the rectangle is perpendicular to the plane of the film. The second, weaker part of the intensity of low-angle scattering consists of two regions of the surface which interconnect the regions of the plane surfaces. These surface regions do not surround the regions of the planes from all sides. They connect the long sides of the rectangles only. All of the low-angle scattering distributions are shown in Figure 3. The reciprocal space is shown in this drawing to scale and $H_0 = 0.072\text{Å}^{-1}$ ($\lambda = 1.54\text{Å}$). /1064

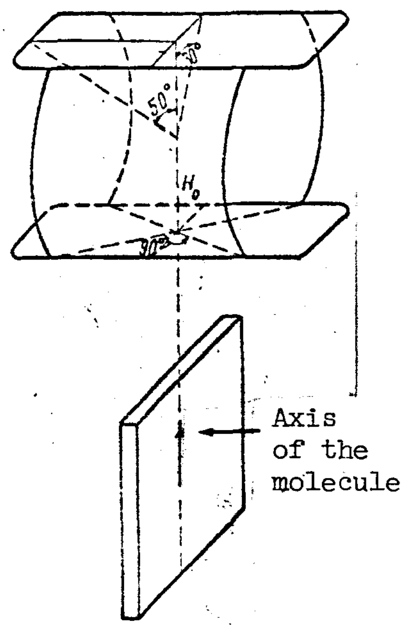

Figure 3. Distribution of Low-Angle Scattering of X-Rays with Respect to the Plane of the Film

Let us see how the form of the inverse space conforms with the intensity distribution on the X-ray pictures of the two series. The region of the plane of the reciprocal space having the form of a rectangle appears in the form of reflexes of various lengths on the X-ray pictures of the first series. In addition, a particularly clear verification of the indicated form of the domain in the reciprocal space is the displacement of the reflex towards large angles on pictures of the second series. During rotation, the regions of the planes in the reciprocal space intersect the sphere of reflection which, for small angles 2 θ may also be replaced by planes at all great distances from the center. This is what produces the displacement of the reflex. Simultaneously, the width of the reflex must decrease along the meridian, and this is also observed on the X-ray pictures (Figure 2a). If the principal part of the intensity were distributed along the Debye ring, then the position of the reflex would not change. Inclined pictures of the type corresponding to the pictures of the second series constitute the most sensitive method for distinguishing the distribution of the intensities along planes in the reciprocal space from the distribution of intensities along the sphere. The nature of the distribution of the second, weaker part of the intensity, which interconnects the regions of planes, is associated with the occurrence of arcs which interconnect the dashes on the layer lines. The fact that the regions of the surfaces interconnect only the long sides of the rectangles is due to the disappearance of the arcs during rotations greater than 45^{o} on the X-ray pictures of the first series. In addition, if the surfaces were to interconnect the planes from all sides, we would have obtained a ring or an elipse in the X-ray pictures of the second series taken with a beam parallel to the plane of the film; i.e., with a beam along the axis of the chain. However, this X-ray picture (Figure 2b) has only two dashes.

In conclusion, we should note that the magnitudes of the angles shown in Figure 3 are approximate with an accuracy of 5^{o} to 10^{o}. A more accurate measurement of these quantities from the low-angle X-ray pictures of the textures is hardly possible.

Discussion of the Results

Let us consider a system of domains having an excess (insufficient) electron density $\Delta\rho$ which is responsible for the occurrence of the large period. In what manner must the domains be distributed along the sample so that we can explain the observed distribution of the intensities of low-angle scattering in the reciprocal space? To explain the absence of the zero layer line there is only one possible proposition--the projection of the excess electron density $\Delta\rho$ on the equatorial plane is the same at all points. This can occur only when each domain, during projection on the equatorial plane, intersects at random. The presence of a well-defined layer line indicates that the projection of the vectors, connecting the domains $\Delta\rho$ and located along the vertical direction, for the most part have a value of 140Å. The intensity of scattering by the domains $\Delta\rho$ may be represented in the form:

$$\Phi^2 \sum_{k,k'} e^{i\bar{s}\bar{r}_{kk'}} = \Phi^2 \sum_{kk'} e^{i\bar{s}_\perp \bar{l}_{kk'}} e^{is_\parallel \eta_{kk'}}.$$

Here, Φ^2 is the scattering of one domain, $r_{kk'}$ is the vector connecting the domains $\Delta\rho_k$ and $\Delta\rho_{k'}$, $S = 4\pi\sin\theta/\lambda$, $S_\parallel$ and $\eta_{kk'}$ are projections of S and $r_{kk'}$ in the vertical direction, and $S_\perp$ and $l_{kk'}$ are the projections of these same vectors on the equatorial plane. The presence of a restrained region in the first plane of the reciprocal space indicates that the value of $l_{kk'}$, which interconnects the domains that produce interference on the first layer line, must lie within the limits which, roughly speaking, are determined by the relationship $I = \pi/S_{rp}$ where S_{rp} corresponds to the maximum value of S_1. This means that the domains Δ_ρ are situated along the chains whose projections on the horizontal plane must be within these limits. /1065

We can propose two models which satisfy this condition and which are shown in Figure 4a and b. However, the existence of a model consisting of linear chains inclined at various angles (Figure 4b) is contrary to experiment.

a b

Figure 4. a. System of Bent Chains; b. System of Linear Chains with Various Inclinations. The black areas represent the crystallites, while the gray areas show the transitions between crystallites.

Indeed, in this case the intensity of the low-angle scattering would have been distributed along a sphere and not along a plane in the reciprocal space as observed experimentally. Thus the only possible scheme is the distribution shown in Figure 4a. The fact that the zero plane in the reciprocal space does not exhibit any low-angle scattering is now easily explained. The chains are bent and intertwine with each other so that the rectangles $\rho_{kk'}$ of the individual chains are superimposed on one another and form a continuous distribution of electron density which naturally does not give any low-angle scattering. These considerations show that a simple analysis of the intensity distribution of low-angle scattering without introducing other data leads to a definite scheme for the distribution of domains in space which are responsible for low-angle scattering.

Let us now discuss in detail the relation between the results of the X-ray investigations carried out with large and small angles. Since the main part of the low-angle scattering intensity is situated on planes perpendicular to the axis of the macromolecule, we are primarily interested in the spatial distribution of the axis of the macromolecules. The distribution of the axes of the chains is characterized by the polar figure H_{-105}, which we shall consider in detail (Figure 5), (Ref. 3).

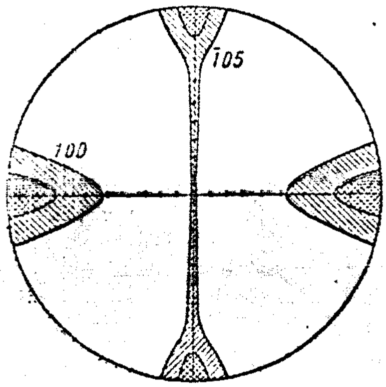

Figure 5. Polar Figures H_{-105} and H_{100}

The polar figure H_{-105} shows that the distribution of the axes of the molecules can be divided into two parts corresponding to the division of the picture of the low-angle scattering intensity. The orientation of the basic part of the axes of the chains is characterized by an ellipse which is strongly elongated in the plane of the film. The second part of the distribution, which is associated with a much smaller number of macromolecular axes, is shown on the polar figure in the form of a narrow strip interconnecting the elongated ends of the ellipses. This part of the polar figure characterizes the axes of the macromolecules which are oriented in an approximately uniform fashion in all directions in the plane of the film. We should remember that the polar figure in Figure 5 is constructed in such a way that the plane of the film intersects it along the meridian.

If we now compare the distribution of the low-angle scattering intensity with the distribution of the orientations of the axes of the macromolecules, it becomes obvious that the principal part of the intensity of low-angle diffraction (i.e., the regions of the planes in the reciprocal space) is associated with the distribution of the basic mass of the macromolecule (i.e., with the ellipse on the polar figure H_{-105}).

The smaller portion of the low-angle scattering intensity, consisting of surfaces connecting the rectangular regions of the planes, is in its turn related with a relatively small quantity of macromolecules oriented in the plane of the film in all directions. /1066

Note that we speak continually of the orientation of the axes of the macromolecules although, strictly speaking, the polar figure characterizes the orientation of the axes of the crystallites. Thus the large period is observed only in the direction of the axis of a macromolecule. In no other direction do we observe the periodicity analogous to the large period.

Let us now consider the asymmetry of the intensity distribution of low-angle scattering along the plane of the reciprocal space; specifically, the rectangular form of the regions of these planes (Figure 3). In what manner can we reconcile this fact with the spatial distribution of crystallites which are characterizes by the polar figure? The dimensions of the ellipse which characterizes the distribution of the basic mass of the macromolecule (Ref. 3) are as follows: in the plane of the film 20°, in the perpendicular direction 10°. Consequently, proceeding from the polar figure, we may say that $l_{kk'}$ must form a rectangle on the equatorial plane whose long side is parallel to the plane of the film and approximately twice the size of its short side which is perpendicular to the plane of the film. Such a distribution of vectors $l_{kk'}$ explains the distribution of the low-angle scattering intensity.

Indeed, from the equality $l = \pi/S_{rp}$ we obtain for $l_{kk'}$ a rectangle 120 Å x 240 Å, whose long side is parallel to the plane of the film. Generally speaking, the nonsymmetric distribution of the intensity may be produced not only by the distribution of $l_{kk'}$ but also by the function Φ^2. However, since the distribution of $l_{kk'}$ obtained from the polar figures well explains the form of the regions of the domains in reciprocal space, we may assume that Φ^2 in this case does not influence the distribution of the intensities along the plane in the reciprocal space. It also follows from this that we cannot use the dimensions of the domain in the reciprocal space to obtain a simple value for Φ^2; i.e., for the form of the domain Δ_ρ. Only when the crystallites are well oriented can we obtain the data on the form of the domains Δ_ρ from the dimensions of the domain in the reciprocal space.

What is the structural interpretation of the results which we have obtained? From the results of investigations with large and small angles, we may say with a fairly firm conviction that the regions between the domains Δ_ρ are individual crystallites, while the domains Δ_ρ themselves represent places where the packets of macromolecules are bent. At the points of bending, the crystalline structure is destroyed and the electron density is reduced. The scheme we obtained confirms the scheme of Hess which explains the origin of the large period by the /1067
alternation of crystalline and amorphous domains along packets of macromolecules. Our results show that the packets of macromolecules must have flexibility (Ref. 4) and that the places at the bends are amorphous domains.

Conclusions

By comparing the orientation of crystallites with the distribution of the intensity of diffraction at small angles, we have made two deductions. First of all, we noted that the large period is only situated along the axis of the macromolecule and is not observed in other directions. Another conclusion concerns the fact that the domains which are responsible for the occurrence of the large period must be places of inflection in the packets of macromolecules and that these inflections are the transitions or boundaries between crystallites of various orientation.

The first conclusion is in agreement with the results of most of the works devoted to the study of large periods, although in some investigations (e.g., Ref. 5), the authors point to the existence of periodicity in directions perpendicular to the axis of the chain and associate these periods with the transverse dimensions of the packets of macomolecules.

On the basis of our results, we may assume that the periodicity discovered along directions which do not coincide with the direction of the basic mass of the macromolecules is associated with the existence of macromolecules and crystallites having a corresponding orientation which is different from the orientation of the basic mass of the chains. These periods must have a small intensity.

The second conclusion is in basic agreement with the scheme of Hess (Ref. 1) which is accepted by most investigators. The packets are bent and are intertwined, which explains the absence of scattering at the zero layer line and which simultaneously makes it impossible, in our case, to determine the transverse dimensions of the packets.

As is known from the literature (Refs. 2 and 6), one of the most interesting facts is the dependence of the large period value on the heat treatment of the sample.

Proceeding from our scheme, the variation in the magnitude of the large period can be explained as a change in the length of the crystallites as well as a change in orientation. This phenomenon together with many other facts concerning the relation between the large period and the variations in structure requires, first of all, a further careful experimental investigation. In the course of such an investigation, in our opinion, it is first necessary to carry on a parallel study of low-angle X-ray pictures and X-ray pictures taken at large angles.

Deductions

1. The distribution of the low-angle scattering intensity of X-rays from films of polyethyleneterephthalate having an axially-plane texture has been studied. A comparison has been made with the results of investigations on the X-ray diffraction of these films for large angles of diffraction.

2. It has been shown that the large period recurrence is observed only along the axis of the macromolecule.

3. It has been made clear that the domains responsible for the occurrence ofthe large period must be areas of transition between crystallites oriented in various directions.

4. It has been shown that the system of bent and intertwined packets of macromolecules explains the picture of the X-ray diffraction for large as well as small angles. /1068

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